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Note

Synthesis and properties of carboxy-substituted half-sandwich ruthenium complexes with chelating bisphosphine ligands $(\eta^5\text{-}C_5H_4CO_2H)Ru(\eta^2\text{-}L)X$ (X = I, H)

Anthony P. Shaw, Hairong Guan, Jack R. Norton *

Columbia University, Department of Chemistry, New York, NY 10027, United States

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Abstract

Several Ru(II) complexes $(\eta^5\text{-}C_5H_4CO_2H)Ru(\eta^2\text{-}L)I$ have been prepared by the hydrolysis of the ester linkage in $(\eta^5\text{-}C_5H_4CO_2\text{-}t\text{-}Bu)Ru(\eta^2\text{-}L)Cl$ with trimethylsilyl iodide. The hydrides $(\eta^5\text{-}C_5H_4CO_2H)Ru(\eta^2\text{-}L)H$ may be prepared by reduction of the iodide complexes in KOH/MeOH solutions followed by acidification. Complexes with several chelating bisphosphine ligands have been prepared in this way. The carboxylate anions $[(\eta^5\text{-}C_5H_4CO_2)Ru(\eta^2\text{-}L)H]^-$ are readily protonated by weak acids to give the carboxyCp complexes. The pK_a of the carboxy proton of $(\eta^5\text{-}C_5H_4CO_2H)Ru(dppe)H$ (dppe = 1,2-bis(diphenylphosphino)ethane) is 11.3 in DMSO. Protonation of the neutral hydride complex $(\eta^5\text{-}C_5H_4CO_2H)Ru(dppf)H$ gives the cationic dihydride $(\eta^5\text{-}C_5H_4CO_2H)Ru(dppf)H_2^+$; the dihydride structure has been confirmed by measuring the T_1 of its ^1H NMR hydride resonance over a range of temperatures. The oxidations of the halide complexes $(\eta^5\text{-}C_5H_4CO_2H)Ru(dppf)I$ and $(\eta^5\text{-}C_5H_4CO_2t\text{-}Bu)Ru(dppf)Cl$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) have been studied by cyclic voltammetry.

Keywords: Ruthenium hydrides; Ester hydrolysis; Carboxy complexes

1. Introduction

Although many complexes with functionalized cyclopentadienyl ligands are known [1], those with carboxy substituents ($C_5H_4CO_2H$ complexes) have not been studied extensively. They should be soluble in aqueous base, allowing catalysts to function in aqueous or biphasic environments. They should be good electrochemical and spectroscopic probes when the carboxy group is attached covalently to biomolecules [2].

Three routes to $C_5H_4CO_2H$ complexes have been reported: (a) Cp ligands can be lithiated and treated with CO_2 [3], (b) $C_5H_4CO_2Me$ complexes can be prepared and the ester saponified [4], and (c) $C_5H_4CO_2H$ complexes can be prepared directly from the free ligand (Thiele's acid) [5,6]. However, we have found that none of these methods work for the preparation of $(\eta^5\text{-}C_5H_4CO_2H)Ru(\eta^2\text{-}L)X$ (Table 1), so we have tried a variant of (b) that avoids strong base: the preparation of complexes of the corresponding *t*-butyl esters and the use of trimethylsilyl iodide to effect their hydrolysis [7].

2. Results and discussion

2.1. Synthesis

The first step (lithiation of a Cp ligand) of approach (a) is sometimes possible in the presence of a hydride ligand: for example, the ring is the kinetic site of lithiation of $CpRe(NO)(PPh_3)H$ with $n\text{-}BuLi/Me_2NCH_2CH_2NMe_2$ at −70 °C [8]. However, approach (a) proved successful with neither $CpRu(CO)_2H$ nor CpRu(dppe)H. We then tried approach (b), after preparing $(\eta^5\text{-}C_5H_4CO_2Me)Ru(dppe)X$

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* Corresponding author. Tel.: +1 2128547644; fax: +1 2128547660.
E-mail address: jrn11@columbia.edu (J.R. Norton).

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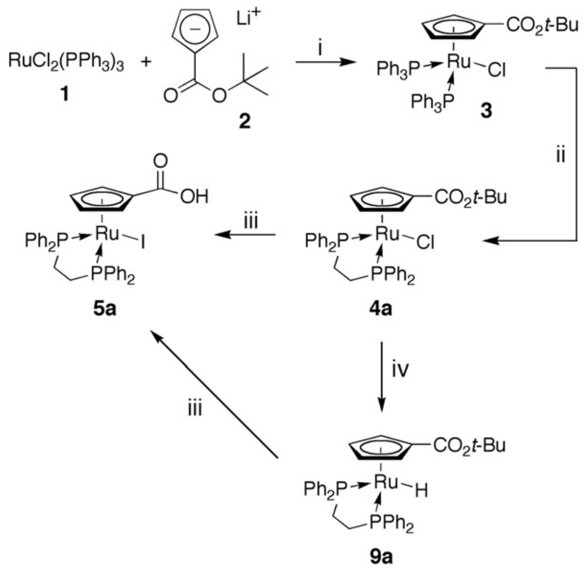
Table 1
(η^5-C_5H_4R)Ru(L)X complexes

Complex	X	R	L
3	Cl	CO_2t-Bu	$(PPh_3)_2$
4a	Cl	CO_2t-Bu	dppe
4c	Cl	CO_2t-Bu	dppf
5a	I	CO_2H	dppe
5b	I	CO_2H	*S*,*S*-CHIRAPHOS
5c	I	CO_2H	dppf
7a	H	CO_2H	dppe
7b	H	CO_2H	*S*,*S*-CHIRAPHOS
7c	H	CO_2H	dppf
8a	H	CO_2^-	dppe
9a	H	CO_2t-Bu	dppe
9c	H	CO_2t-Bu	dppf

(X = Cl, H) [9]. However, numerous attempts to hydrolyze this methyl ester (aqueous base and methanol, acetone, or THF) failed, as did an attempt to hydrolyze the ester linkage in (η^5-$C_5H_4CO_2Me$)Ru$(PPh_3)_2$Cl with trimethylsilyl iodide. (Trimethylsilyl iodide can be used to hydrolyze some methyl esters, although the reactions are often slow [7].) We then tried approach (c), but were unable to prepare $C_5H_4CO_2H$ complexes by the reaction of Thiele's acid with $Ru_3(CO)_{12}$ or $RuCl_3 \cdot 3H_2O$/phosphines [10].

Eventually we made the bis(triphenylphosphine) ruthenium chloride complex **3** by treating $RuCl_2(PPh_3)_3$ (**1**) with Li[$C_5H_4CO_2t$-Bu] (**2**) [11] in refluxing THF (Scheme 1). Treating **3** with dppe in refluxing toluene replaced the triphenylphosphines with dppe, giving the *t*-butyl ester chloride complex **4a**. Treating **4a** with NaOMe in MeOH gave (η^5-$C_5H_4CO_2t$-Bu)Ru(dppe)H (**9a**). The latter decomposed under the acidic conditions (aqueous HCl/CH_2Cl_2) needed to hydrolyze the ester, but gave **5a** when treated with excess trimethylsilyl iodide followed by water. We therefore treated **4a** with excess trimethylsilyl iodide in CH_2Cl_2, and found that it also gave **5a** after treatment with water [7]. The exchange of chloride with iodide is not surprising given the lability of halide ligands in such complexes [12].



i. THF, Δ
ii. dppe, PhMe, Δ
iii. (1) Me_3SiI, CH_2Cl_2 (2) H_2O
iv. NaOMe, MeOH, Δ

Scheme 1.

Refluxing **5a** with KOH in methanol afforded a light yellow solution of the $C_5H_4CO_2^-$ hydride complex **6a** (Scheme 2). The addition of benzoic acid gave the carboxy complex **7a** in solution, while the addition of benzamidine hydrochloride gave the salt **8a**. Both hydride complexes precipitated after the addition of water.

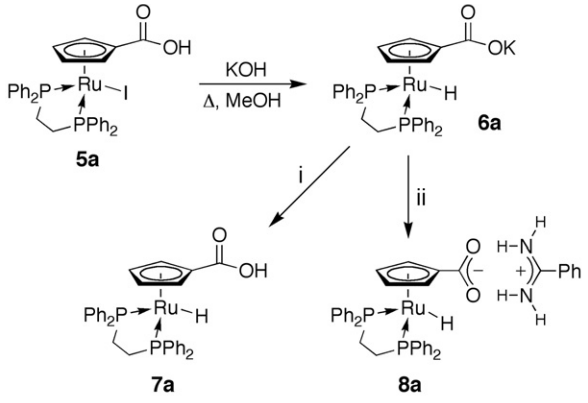
These methods have proven readily adaptable to Ru complexes of other bisphosphines. The complexes in Table 1 have all been prepared by procedures like those in Schemes 1 and 2.

2.2. Properties and reactivity

Although their analogs with unsubstituted cyclopentadienyl ligands are quite soluble in CH_2Cl_2, the orange-red $C_5H_4CO_2H$ ruthenium iodides **5a**, **5b**, and **5c** are much more soluble in DMSO than in halogenated solvents (the iodide **5a** is only sparingly soluble in methylene chloride). The difference is presumably the result of hydrogen bonding between the carboxy substituents and DMSO [13]. The yellow hydrides (**7a**, **7b**, **7c**, and **8a**) behave similarly. None of the carboxyCp complexes are particularly sensitive to oxygen; in the solid state they can be handled in air.

The ^1H NMR spectra of the carboxyCp complexes **5** and **7** in DMSO-d_6 all display broad peaks that range from δ 11.43 to 12.49 for their carboxy protons. The hydride ligands in **7** show well-resolved triplets that range from δ −13.96 to −12.75, with no evidence of any interaction between these ligands and the carboxy protons (at least in DMSO).

Treatment of the benzamidinium salt **8a** with 1 equiv. of $HBF_4 \cdot OMe_2$ in DMSO-d_6 gave only the carboxyCp com-



i. benzoic acid, H_2O
ii. benzamidine hydrochloride, H_2O

Scheme 2.